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CHEMICAL TRANSFORMATIONS IN ACID RAIN

Volume II. Investigation of Kinetics and Mechanism of Aqueous-Phase Peroxide Formation

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16. ABSTRACT

The aqueous-phase reactions of O_3 with a number of species have been studied in an effort to identify pathways leading to the production of hydrogen peroxide in solution. The aqueous-phase systems studied included the decomposition of O_3 in pure water and the interaction of O_3 with (1) NO_2, (2) PAN, (3) ethylene, (4) formic acid, (5) formaldehyde and (6) formaldehyde in the presence of NO_2. Except for the O_3-ethylene reaction, peroxide was not found as a reaction product. From the results obtained, it is concluded that the reactions studied in this research effort are not significant with respect to atmospheric peroxide formation.

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ABSTRACT

The aqueous-phase reaction kinetics of dissolved O_3 with a number of atmospheric components have been investigated, with special attention focused on the formation of H_2O_2 or organic peroxide as reaction products. The reagent concentrations employed, rate laws, rate constants, and peroxide yields (y) determined for the specified substrates are:

H_2O: $-d[O_3]/dt = k[O_3]$, $k = 2.1 \times 10^{-4}$ s^{-1} (pH ~6), $y \leq 0.5\%$;

H_2O_2 ($\sim 5 \times 10^{-5}$ M): $-d[O_3]/dt = -d[H_2O_2]/dt = k[O_3][H_2O_2]$, $k = 2.6 \times 10^{3}$ M^{-1} s^{-1} (pH ~6);

HCO_2H ($\sim 1 \times 10^{-5}$ M): $-d[O_3]/dt = k[O_3][HCO_2^-]$, $k = 4.3 \times 10^{3}$ M^{-1} s^{-1}, $y < 0.5\%$;

H_2CO ($\sim 1 \times 10^{-5}$ M): $-d[O_3]/dt = k[O_3]^{1/2}\,[H_2CO]^{1/2}$, $k = 1.2 \times 10^{-3}$ s^{-1}, $y < 2\%$;

C_2H_4 (~15 ppm): $d[\text{peroxide}]/dt = k[O_3][C_2H_4]$, $k = 3.0 \times 10^{5}$ M^{-1} s^{-1};

PAN (~100 ppb): $d[\text{peroxide}]/dt = k[PAN][O_3]$, $k \leq 3 \times 10^{3}$ M^{-1} s^{-1};

NO_2 (40 ppb): $d[\text{peroxide}]/dt = k\,H_{NO_3}P_{NO_3}$, $k\,H_{NO_3} \leq 4 \times 10^{-3}$ M atm^{-1} s^{-1};

$NO_2 + HCO_2$ (1×10^{-4} M): $d[\text{peroxide}]/dt = k\,H_{NO_3}[H_2CO]P_{NO_3}$, $k\,H_{NO_3} \leq 6$ atm^{-1} s^{-1}.

With the use of these data, the rates of the aqueous-phase peroxide production of these reactions under typical atmospheric conditions are calculated to be $\sim 1 \times 10^{-6}$ M hr^{-1} or smaller. It is therefore concluded that the reactions studied in this work contribute insignificantly to the formation of peroxides in atmospheric water.

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INTRODUCTION

The major acids found in the rain and precipitation, namely, sulfuric acid and nitric acid, are believed to be derived from SO_2 and NO_x emitted mainly from the burning of fossil fuel by power plants, smelters, mobile sources, and space heating. The production of final acids from their precursors in the atmosphere involves chemical transformation in conjunction with transport and deposition. In order to formulate an efficient strategy to control the amount of acid deposition and to minimize its environmental impact, a thorough understanding of each of these atmospheric processes has to be acquired.

It has been recognized that the chemical reactions which produce the strong acids can take place either in the gas phase or in the liquid phase. This notion was established because convincing evidence has been collected to indicate that the atmospheric oxidation of SO_2 is strongly affected by aqueous-phase reactions, particularly by ozone and hydrogen peroxide (Penkett et al., 1979; Martin, 1983; Kelly et al., 1984). In order to assess the importance of these aqueous reactions, the atmospheric concentrations of O_3 and H_2O_2 have to be determined. Although the gas-phase concentration of ozone can be accurately determined by various techniques such as ethylene-chemiluminescence, no viable method is currently available for the measurement of gas-phase concentrations of H_2O_2. As a result, the major gas-phase routes for peroxide generation, i.e., the recombination of hydroperoxy radicals and the photolysis of formaldehyde, cannot be confidently employed in a numerical model as the sole source for this species. Furthermore, recent attempts to determine the gas-phase concentrations of peroxide using bubbler series have revealed the existence of <u>in-situ</u>

production of artifact peroxide (Heikes, 1984; ten Brink et al., 1984; Heikes et al., 1982). This observation suggests that aqueous pathways for peroxide formation might exist, in addition to gas-phase counterparts. Clearly, these pathways have to be identified and characterized before it is possible to accurately model the atmospheric budget of H_2O_2 and the rate of SO_2 oxidation.

Among the various potential precursors of aqueous peroxide, it has been speculated that O_3 might be a plausible candidate based on the following considerations: (1) O_3 produces peroxides upon reaction with certain organic compounds, e.g., olefins (Gilbert, 1976), (2) aqueous-phase O_3 reactions were found to involve free radicals derived from O_3 decomposition that might serve as H_2O_2 precursors (Hoigne and Bader, 1976; Bühler et al., 1984), and (3) the bubbler series experiments (Heikes et al., 1982) demonstrated that the levels of artifact H_2O_2 do not diminish rapidly along the bubbler train, consistent with the presumption that the precursor species might be present in relatively high concentration and has a low aqueous solubility. O_3 appears to fit the description.

Although the aqueous-phase reactions of ozone have been the subject of numerous studies for the past several decades, major gaps exist in the understanding of the detailed features of these reactions. Additionally, with the emphasis focused on drinking water treatment by O_3, no major efforts have been directed to the product analysis, particularly H_2O_2. In this current laboratory research we have examined a series of aqueous-phase reactions of O_3 and the formation of H_2O_2 and organic peroxides as their reaction products in an attempt to identify the direct aqueous sources of peroxides. The aqueous-phase reaction systems examined include: (1) O_3

self-decomposition, (2) O_3 reaction with formaldehyde (with and without the presence of NO_2), formic acid, ethylene, and peroxyacetyl nitrate (PAN). Except for the O_3-ethylene reaction, peroxide was not found as a reaction product. From this study it is concluded that the reactions studied here are not significant with respect to atmospheric peroxide formation. As a result, knowledge of direct aqueous-phase sources of H_2O_2 remains highly uncertain.

EXPERIMENTAL

Material

N_2 (Ultra-High Purity, Linde) and O_2 (Ultra-Zero, Matheson) which contained less than 0.5 ppm hydrocarbons (as CH_4) were used as the diluent gas and O_3 source, respectively. NO_2 gas was prepared using a NO_2 permeation device (Metronics, Inc., wafer type) enclosed in a constant temperature oven. With a 15 cc/min flow of N_2 carrier gas the concentration of NO_2 from the permeation source was determined to be 6.0 ppm. Samples of gaseous PAN (6-12 ppm) in N_2 were prepared from concentrated PAN stock solution in n-tridecane prepared according to a modified method of Nielsen (Nielsen et al., 1982; Gaffney et al., 1984). Working stock of ethylene (0.140%) in N_2 was prepared from pure ethylene (99.5%, Scott) and UHP N_2. H_2O_2 (30%), H_2CO (37%) and HCO_2H (88%), all of reagent grade from either Mallinckrodt or Baker, were used without purification. EDTA, Trisma Base, and horseradish peroxidase were of the highest purity available from Sigma Chemical Company. Concentrated HCl and NaOH and inorganic salts such as KCl were all of reagent grade and used without further purification. Fresh solutions of standards and reagents were prepared for the same-day use. Distilled water (resistance $\geq$ 16 Mohm at 25°C), which had been further purified by Millipore Milli-Q System, was used for all of the studies.

Ozone Generation

Two ozone generators were used. For higher O_3 output (up to ~200 ppm at 1 ℓ/min flow rate) a 10-inch Pen-Ray UV lamp was employed. This source was used mainly for the preparation of saturated O_3 solutions for batch-type reactions. For lower O_3 output, an AID Ozone Generator (Model 565) equipped

with a continuously adjustable shutter for O_3 output control was employed (up to ~1 ppm at 1 ℓ/min flow). This source was used for the continuous-flow reaction system. For both generators, high purity O_2 purchased from Matheson was used in order to minimize possible interferences from NO_x and organic impurities.

Gas-Phase O_3 Concentration

Gas-phase O_3 concentrations were determined either by a Dasibi O_3 monitor (Model 1008-PC) operated based on UV absorption (LOD ~2 ppb) or by a Monitor Labs Ozone Analyzer (Model 8410) based on the O_3-ethylene chemiluminescence, with the former as the primary standard.

Preparation of O_3 Solution

For batch-type experiments, O_3 solutions were prepared in a 2-liter bubbler through which O_3 was continuously bubbled at a total O_2 flow of 70 cc min^{-1} (Fig. 1). Each Pyrex O_3 bubbler (volume ~2 ℓ) was equipped with a coarse-sized frit for the enhancement of mixing and with two ports for liquid transfer. The plumbing was constructed with parts made either of stainless steel or Teflon for purity. Bubbler 1 was needed for the humidifying of the gas-stream and the removal of any soluble substances; bubbler 2 supplied saturated O_3 solutions to be used for the batch studies. For the study of some continuous-flow reactions, valve M-1 was switched so that O_3 would flow through the gas-liquid reaction cell to initiate the reactions.

Aqueous-Phase O_3 Concentration

The concentration of aqueous-phase O_3 was measured by a UV-vis spectrophotometer (Beckman Model DU-7) using either a 10 cm or a 5 cm cylindrical

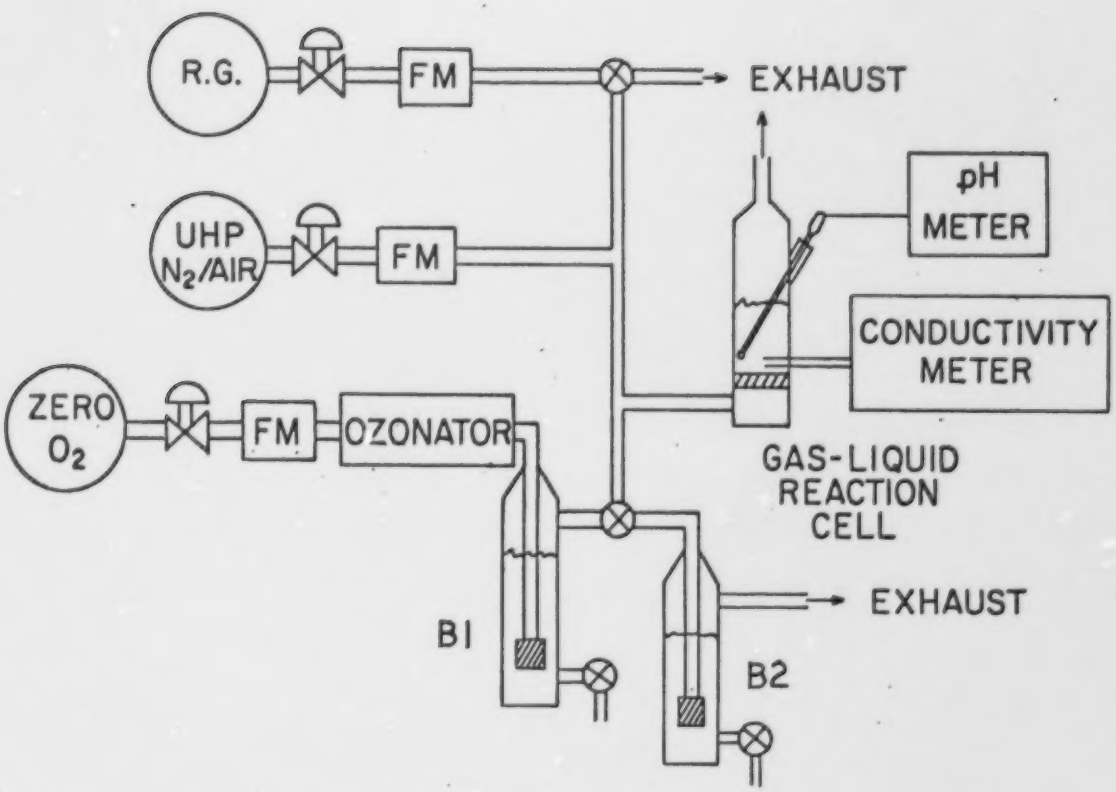

Figure 1. Schematic diagram of the experimental setup.

optical cell. Spectra of the O_3 solutions in the bubbler were taken during the saturation process (Fig. 2) and the concentrations of O_3 were determined from the absorption peak at 260.0 nm using an extinction coefficient ϵ = 2930 M^{-1} cm^{-1} (Kosak-Channing and Helz, 1983). The time dependence of O_3 saturation in the 2-liter bubbler is shown in Figure 3. Using the 10-inch Pen-ray UV ozonator at O_2 flow rate of 70-90 cc min^{-1}, a typical aqueous-phase O_3 concentration of 1-2 x 10^{-5} M was obtained after 40 min of bubbling. The limit of detection for O_3 with the use of the 10-cm cell is 1 x 10^{-7} M.

H_2O_2 and Organic Peroxide Concentrations

Concentrations of aqueous-phase H_2O_2 and organic peroxides were determined by the horseradish peroxidase-fluorescence technique (HRPF) (Guilbault et al., 1968) modified by NCAR (Lazrus et al., 1983). In our arrangement, a Perkin-Elmer fluorometer (Model 204S) was employed in conjunction with a liquid flow reaction system equipped with a rotary injection valve (Altex, sample loop size 0.5 ml). The limit of detection of the HRPF technique is 1 x 10^{-7} M. Since this technique does not distinguish organic peroxides from inorganic H_2O_2, the determination of the concentration of organic peroxides was achieved by a difference method in which H_2O_2 is preferentially destroyed (or inactivated) by the enzyme catalase (Schonbaum and Chance, 1976).

Kinetic Measurements

Two different types of kinetic methods were used. In the batch-type study, reactions were initiated by mixing the reagents with O_3 solution in an optical cell and the decrease of $[O_3]$ accompanying the reactions were

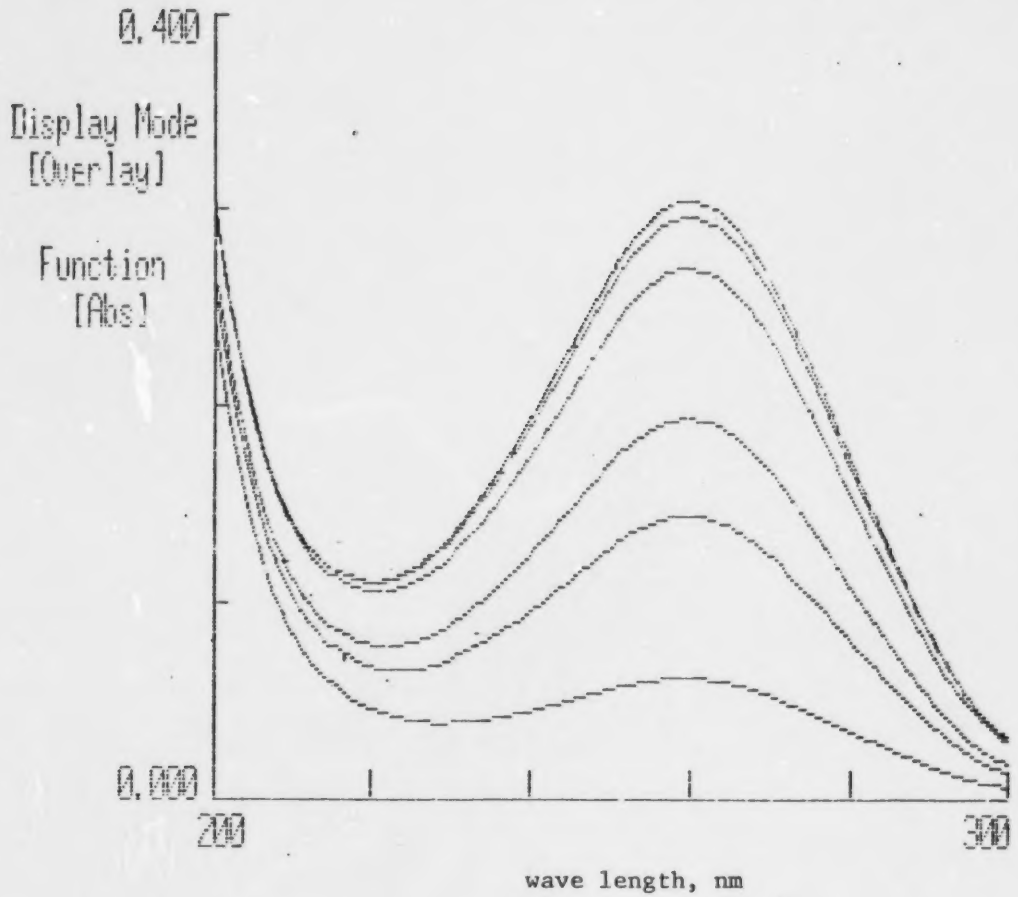

Figure 2. Aqueous-phase O_3 spectra, taken during the course of saturation process.

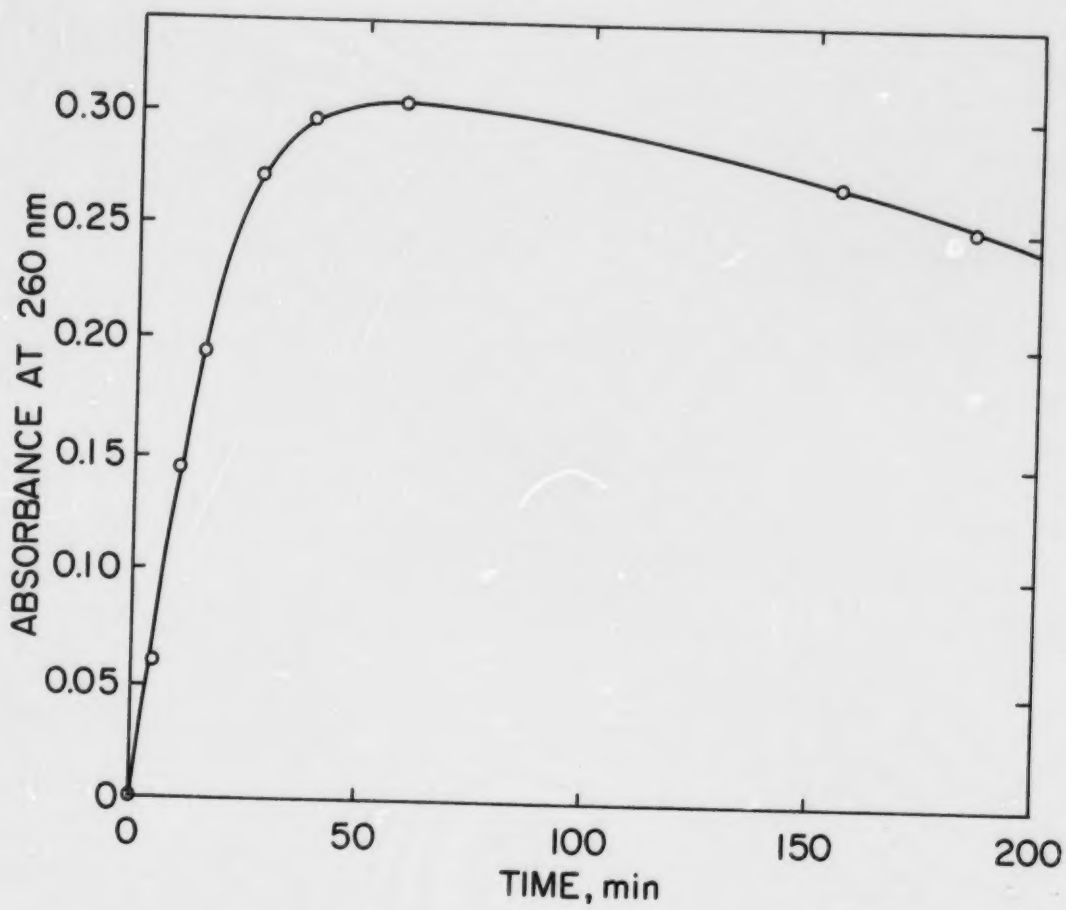

Figure 3. Time dependence of the O_3 saturation in a 2-liter bubbler. Flow of O_2 = 70 cc min^{-1}.

followed spectrophotometrically at λ = 260 nm. In the continous-flow reaction, a reagent gas mixture containing constant concentrations of O_3 and other gaseous reactants was continuously bubbled through a solution contained in a bulk-type gas-liquid reactor. The detailed construction of the gas-liquid reactor is shown schematically in Figure 4. The kinetics of H_2O_2 generation were followed by an aliquot method in which H_2O_2 concentrations were determined by the HRPF technique. Temperature of the reaction vessel was maintained at 22.0 $\pm$ 0.1°C for the latter method, but for the spectrophotometric technique the uncertainty was somewhat greater ($\pm$2°C) due to the lack of temperature control of the sample compartment for a cylindrical cell.

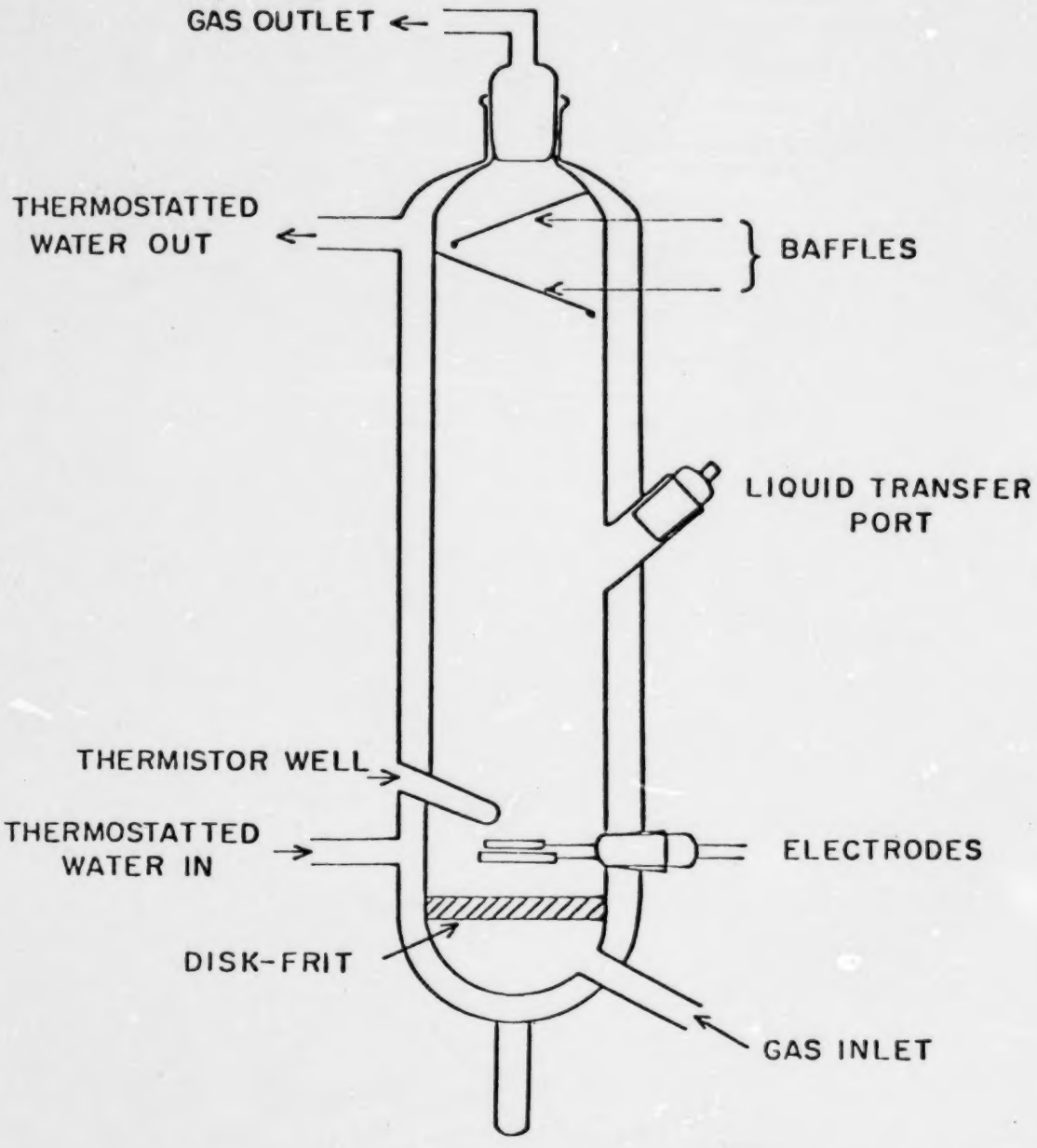

Figure 4. Schematic of the construction of a bubbler-type gas-liquid reaction vessel.

RESULTS

O_3 Decomposition in Optical Cell

In order to study the reaction kinetics of O_3 with other substrates using a spectrophotometric method, it is necessary to determine the stability of O_3 solution in the optical cell employed. Figure 5 shows a typical decay curve of O_3 in a 5 cm cylindrical cell under neutral pH (no acid or base added). The first-order rate constant was found to be 2.1×10^{-4} s^{-1}. When pH of the solution was adjusted to 2 by HCl the rate constant of O_3 decomposition dropped to 1.4×10^{-4} s^{-1}. These values were repeatable within 15% and were found to be slow compared to other O_3 reaction.

The final decomposition mixture of the O_3 solutions (containing initial $[O_3]$ as high as 2.0×10^{-5} M) was analyzed for H_2O_2. The concentration of H_2O_2 was found to be below the limit of detection of 1×10^{-7} M.

O_3 - H_2O_2 Reaction

In order to examine possible H_2O_2 formation in O_3 reactions, the reaction between O_3 and the reaction product, H_2O_2, should be quantified. The kinetics of this reaction was studied under pseudo-first-order condition, i.e., $[H_2O_2]_0 \gg [O_3]_0$. A typical trace of O_3 decomposition under such a condition is shown in Figure 6. The O_3 decay kinetics was found to conform to a pseudo-first-order reaction for ~3 half-lives. The second-order rate constant, obtained by dividing the pseudo-first-order rate constants by $[H_2O_2]_0$, which had been varied from 8×10^{-6} M to 6.4×10^{-5} M, was determined to be $(2.6 \pm 0.4) \times 10^3$ M^{-1} s^{-1} at neutral pH. The good agreement obtained between the second-order rate constants determined at widely different H_2O_2 concentrations permits the conclusion that the reaction kinetics are also first order with respect to $[H_2O_2]$. At lower pH the

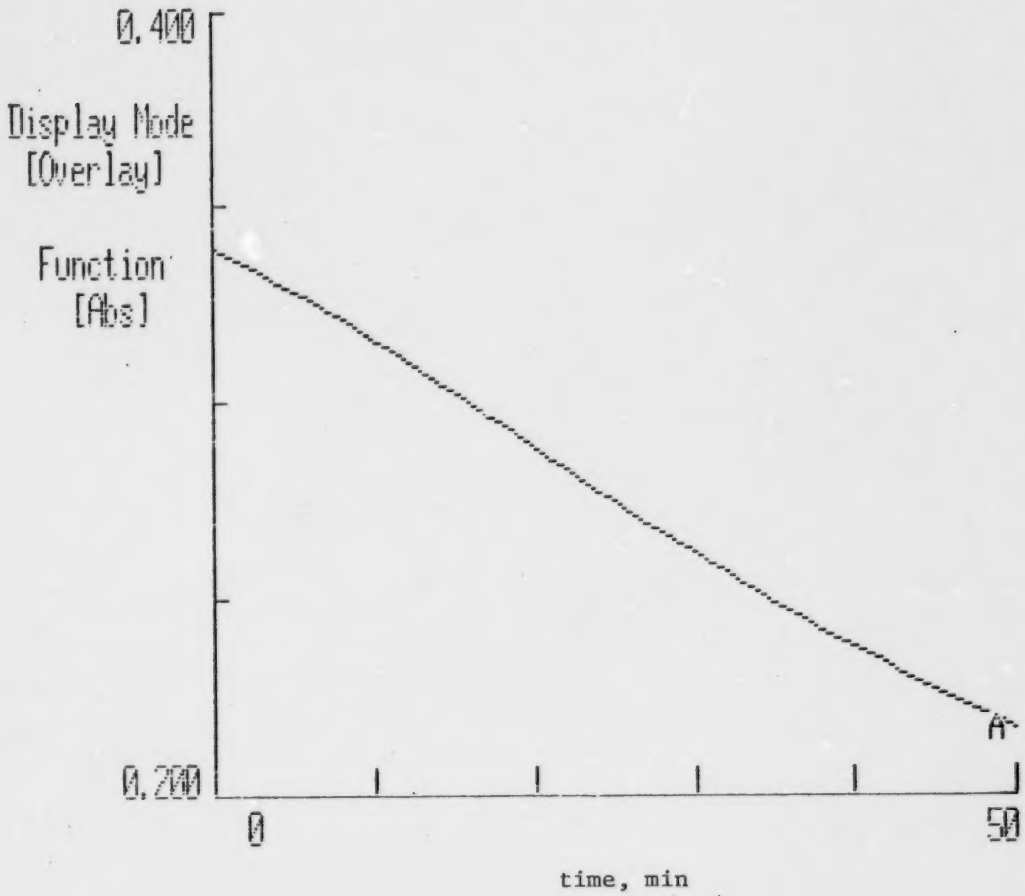

Figure 5. Kinetics of O_3 decomposition in a 5 cm cylindrical quartz optical cell.

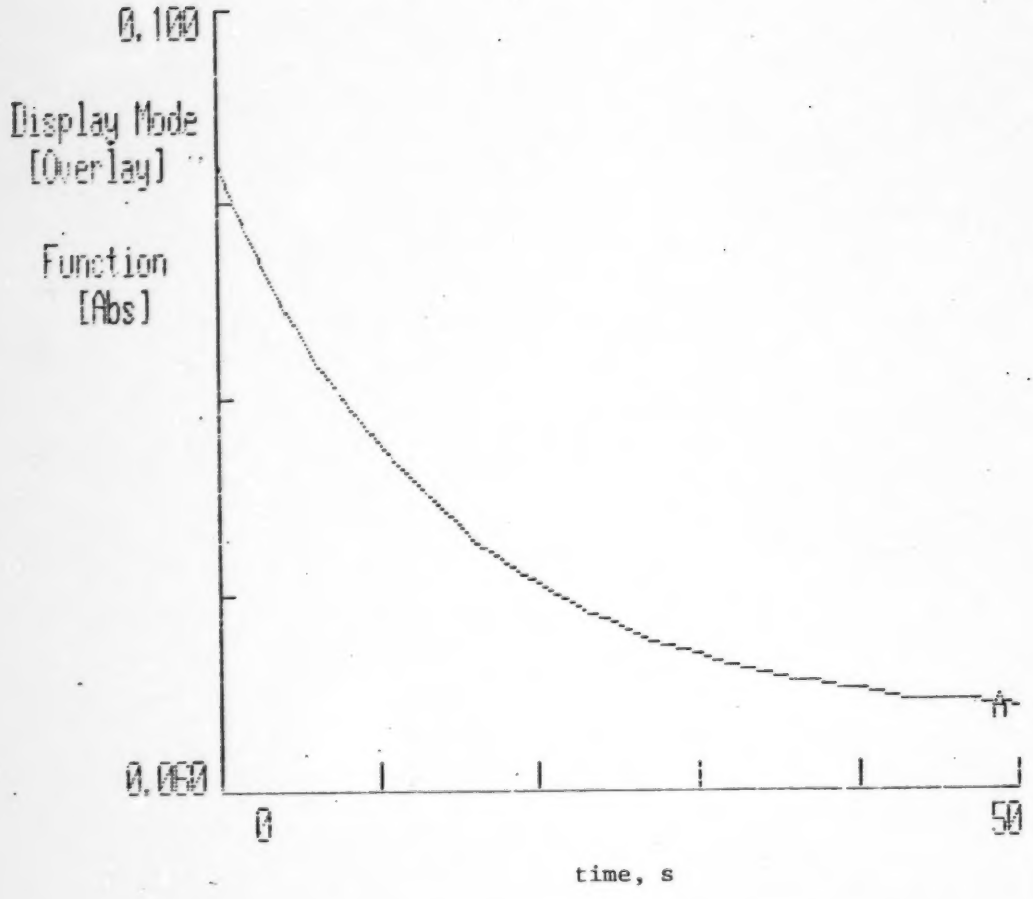

Figure 6. Time dependence of O_3 disappearance due to reaction with H_2O_2. Initial concentrations of H_2O_2 and O_3 were 3.5×10^{-5} M and $\sim 4 \times 10^{-6}$ M, respectively.

reaction rate decreased rapidly. A second-order rate constant of 38 ± 8 M^{-1} s^{-1} was determined at pH = 4, where the solutions contained [HCl] = 1.00 x 10^{-4} M.

O_3 - HCO_2H Reaction

Formic acid has been identified as a major organic acid component in rainwater (Keene et al., 1983) and therefore the sources and sinks of this species may be of importance to the understanding of acid rain formation mechanisms. We examined the aqueous-phase reaction of O_3 with HCO_2H to determine the reaction rate and the yield of peroxide as a product.

$$O_3 + HCO_2H \xrightarrow{k_1'} \text{Products} \qquad (1)$$

The kinetic study of reaction (1) was made by monitoring the change of $[O_3]$ followed spectrophotometrically at λ = 260 nm. Since the rate of this reaction under current conditions is too fast to be studied under pseudo-first-order condition, i.e., high concentrations of HCO_2H, initial concentrations of O_3 and HCO_2H were made approximately equal at ca. 2 x 10^{-5} M. Treating the reaction with an overall second-order kinetics, i.e.,

$$\text{Rate} = \frac{-d[O_3]}{dt} = k_1'[O_3][HCO_2H] \qquad (2)$$

the rate constant was determined by using a second-order plot

$$\frac{1}{[O_3]_t} - \frac{1}{[O_3]_0} = k_1't \qquad (3)$$

Plots of $[O_3]_t^{-1}$ vs. time were found to be linear for at least three half-lives. A typical run is shown in Fig. 7. The rate constants obtained are listed in Table 1 as a function of pH.

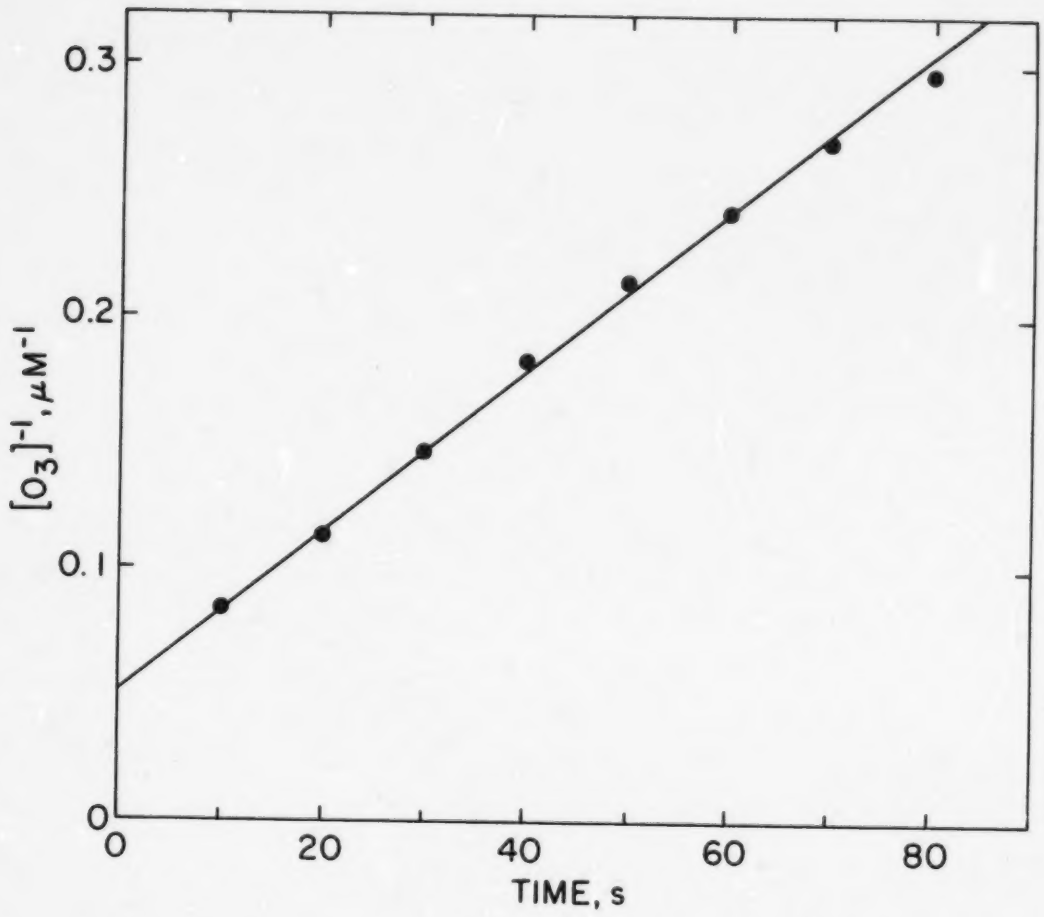

Figure 7. Plot of a second-order kinetics of O_3 - HCO_2H reaction at neutral pH and $[O_3]_0 \cong [HCO_2H]_0 = 2 \times 10^{-5}$ M.

Table 1
Second-Order Rate Constant of O_3 - HCO_2H Reaction at 25 ± 2°C

pH	k_1', M^{-1} s^{-1}
3.00 ± 0.02	$(2.5 \pm 0.2) \times 10^2$
4.00 ± 0.05	$(1.8 \pm 0.2) \times 10^3$
4.60 ± 0.2	$(3.3 \pm 0.5) \times 10^3$

The pH dependence of k_1', increasing with higher pH, can be fitted to a rate law which assumes the rate determining step involves O_3 and the dissociated formate ion, i.e.,

$$\text{Rate} = k_4 [O_3][HCO_2^-]$$

$$= k_4 \left(\frac{K_a}{[H^+] + K_a}\right) [O_3][HCO_2H]_T$$

$$= k_1'[O_3][HCO_2H]_T \qquad (4)$$

where K_a is the acid dissociation constant of formic acid and $[HCO_2H]_T$ is the total analytical concentration of formic acid. Fitting Eq. (4) to the experimental data allowed the values of k_4 and K_a to be determined; they were found to be 4.3×10^3 M^{-1} s^{-1} and 8.9×10^{-5} M^{-1}, respectively.

Although the agreement between the data and the calculated curve appears to be quite reasonable (Fig. 8), the pK_a value of formic acid determined here, 4.1 ± 0.1, is nearly 0.3 unit higher than the literature value of 3.75 (Riddick and Bunger, 1970). While this discrepancy may be acceptable in view of the fact that the kinetic approach generally would yield a larger uncertainty for pK_a determination (Sillen and Martell, 1964) than

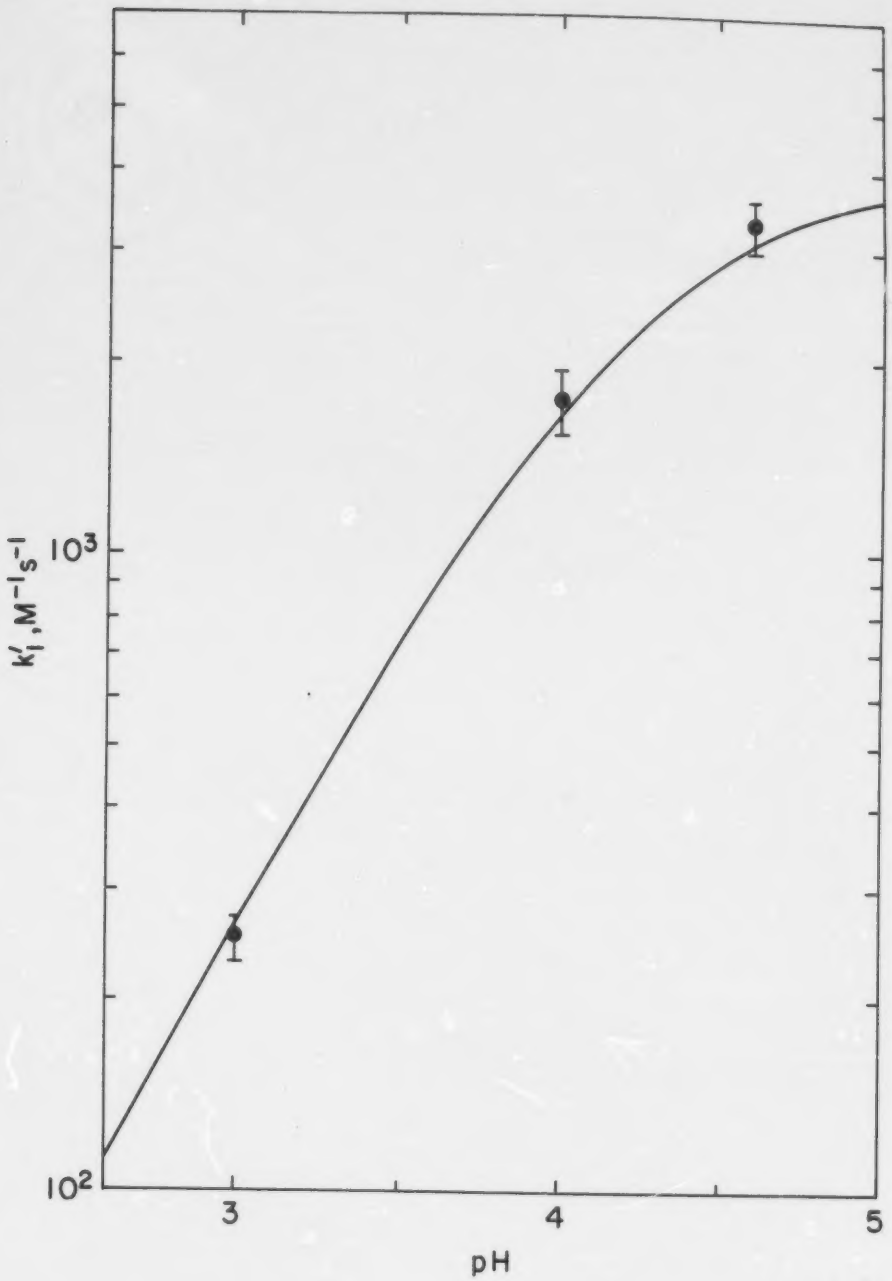

Figure 8. Plot of the pH dependence of the second-order rate constants for O_3 - HCO_2H reaction

other methods (e.g., conductometric), we nonetheless consider this base-catalyzed mechanism tentative.

Final reaction mixtures of the O_3-HCO_2H reaction were analyzed for peroxide by the HRPF method. The level of peroxide was found to be smaller than the LOD of the instrument, namely, 1×10^{-7} M. Under the present reaction conditions, e.g., $[O_3]_0 = [HCO_2H]_0 = 2 \times 10^{-5}$ M, a value of 0.5% is estimated as the upper limit for the peroxide yield of the O_3-HCO_2H reaction.

O_3 - H_2CO Reaction

Since formaldehyde is a relatively abundant atmospheric organic constituent (Grosjean, 1982; Tanner and Meng, 1984) which is derived mainly from combustion emission and the atmospheric oxidation of higher hydrocarbons, its chemistry is of considerable interest to the understanding of atmospheric oxidant formation mechanisms. The aqueous-phase reaction of O_3 with H_2CO was studied in a similar fashion to the O_3-HCO_2H reaction, namely, the extent of the reaction in a 5-cm optical cell was monitored by UV absorption for $[O_3]$ decrease.

The kinetics, under conditions where initial $[H_2CO]$ was in large excess of $[O_3]$, did not conform to a pseudo-first-order reaction. In fact, the effective second-order rate constant appeared to increase as $[O_3]$ was decreasing, indicating a reaction order of less than unity with respect to O_3. This behavior is illustrated by a typical run shown in Figure 9 where $[H_2CO]_0 = 1.65 \times 10^{-4}$ M and $[O_3]_0 = 1.75 \times 10^{-5}$ M.

Since it has been shown that formic acid is produced as a product in the O_3-H_2CO reaction (Kuo and Wen, 1977), i.e.,

$$O_3 + H_2CO \rightarrow O_2 + HCO_2H \qquad (5)$$

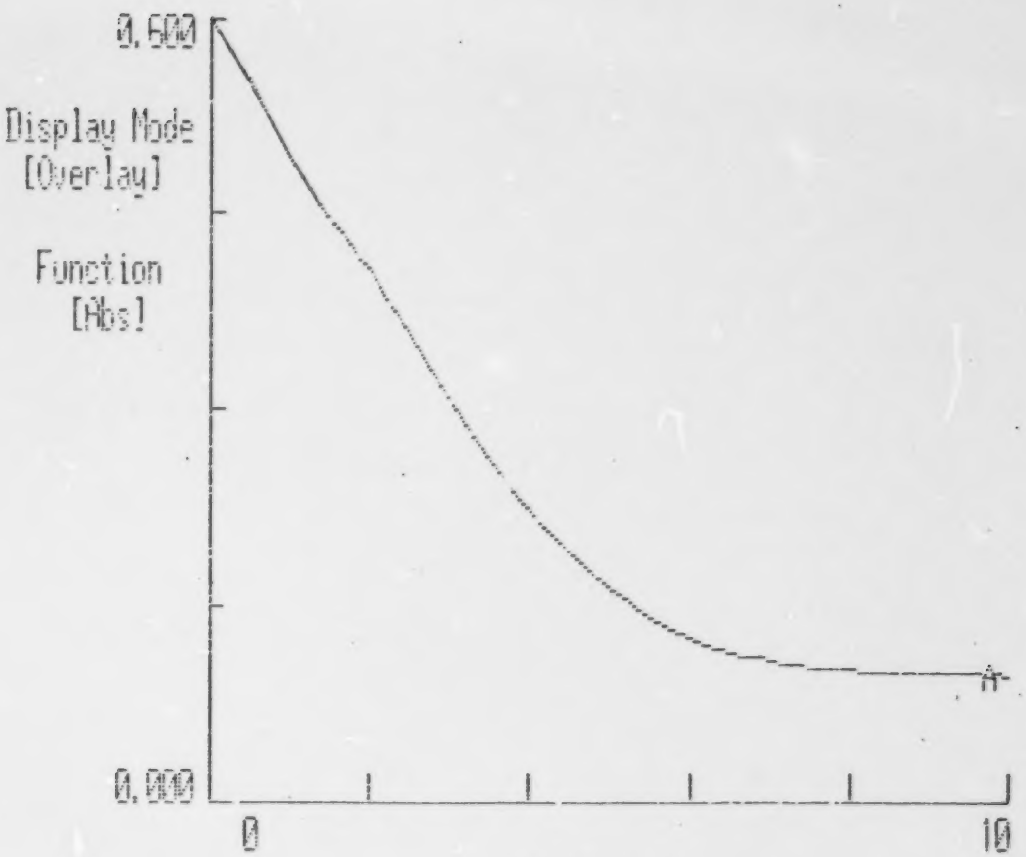

Figure 9. Time dependence of O_3 disappearance due to the reaction with H_2CO. Initial concentrations of H_2CO and O_3 were 1.65×10^{-4} M and 1.7×10^{-5} M, respectively.

the O_3 decomposition may be enhanced by the subsequent O_3-HCO_2H reaction, thereby manifesting a non-first-order kinetics. Comparing the initial rates of the O_3- H_2CO reaction with that for O_3- HCO_2H reaction indicated that the O_3 decomposition due to the secondary reaction with the intermediate product, HCO_2H, can be significant, if HCO_2H is indeed produced stoichiometrically. However, since the product analysis reported by Kuo and Wen '1977) did not appear to be quantitative and it is not clear to us whether or not formic acid is produced from an elementary reaction step, we analyzed our experimental data without invoking the reaction of HCO_2H, but strictly in terms of O_3 and H_2CO. It should be noted that the general kinetic behavior so deduced may be applied only to reaction conditions similar to that employed in this study.

To determine the reaction order with respect to each of the reagent concentrations, we consider the equation

$$\text{Rate} = \frac{-d[O_3]}{dt} = k[O_3]^n[H_2CO]^m \qquad (6)$$

Under conditions that $[H_2CO]_0 >> [O_3]_0$, Eq. (6) is rearranged to yield

$$(\text{Rate}/[H_2CO]^m) = k\,[O_3]^n \qquad (7)$$

where $[H_2CO]^m$ is a constant throughout the reaction course. Taking logarithm of Eq. (7), we obtain

$$\log\,(\text{Rate}/[H_2CO]^m) = \log k + n \log [O_3] \qquad (8)$$

Fitting Eq. (8) to the data obtained from Figure 9 (from which a set of Rate vs. $[O_3]$ can be determined for any specified time), the value of the slope,

n, was found to be ~1/2 (Fig. 10). Using the same approach, an analogous equation is obtained as

$$\log (\text{Rate}_0/[O_3]^{1/2}) = \log k + m \log [H_2CO]_0 \qquad (9)$$

To determine m, we measured the initial rate for three initial formaldehyde concentrations: $[H_2CO]_0 = 1.65 \times 10^{-4}$ M (Fig. 9), 8.2×10^{-5} M, and 4.1×10^{-5} M. Fitting Eq. (9) to the rate data, m was found to have a value also close to 1/2 (Fig. 10). Eq. (6) is now tentatively identified as

$$\text{Rate} = k [O_3]^{1/2} [H_2CO]^{1/2} \qquad (10)$$

with $k = (1.15 \pm 0.7) \times 10^{-3}$ s^{-1}, at $t = 20 \pm 2^{\circ}C$, for the reaction conditions employed.

Product analysis of the final reaction mixtures showed that H_2O_2 was a minor product. With $[H_2CO]_0 = 8 \times 10^{-5}$ M and $[O_3]_0 = 8 \times 10^{-6}$ M the H_2O_2 formed was found to be 1.5×10^{-7} M at the conclusion of the reaction.

O_3-C_2H_4 Reaction

Olefins represent an important class of organic constituents of the atmosphere because of their reactivity towards O_3 and OH oxidation (Niki et al., 1983). Since the Criegee intermediates formed in O_3-olefin reactions may transform into peroxides in protic solvents, we have examined the kinetics of the aqueous O_3-ethylene reaction in connection to its rate of peroxide production. Due to the low solubility of C_2H_4, i.e., $H_{C_2H_4} = 5.0 \times 10^{-3}$ M atm^{-1} at 25°C (Wilhelm et al., 1977), the kinetics of this reaction was studied by the use of the continuous-flow method. A constant flow of N_2 (typically 2.0 ℓ min^{-1}) was first allowed to flow through the gas-liquid

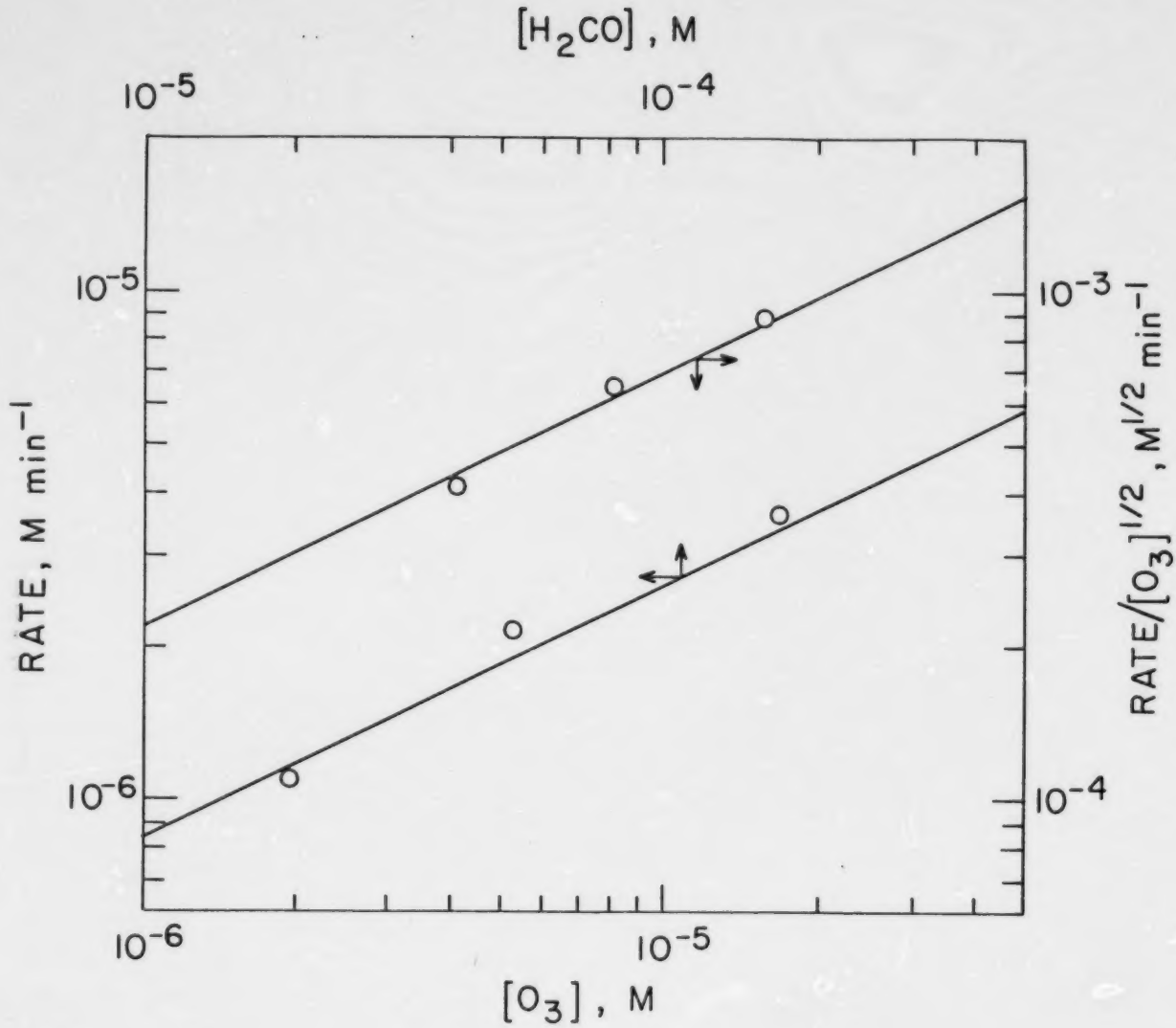

Figure 10. Reaction order determination for H_2CO-O_3 reaction. Plots were made according to eq. 8 and eq. 9. See text for definitions.

reaction cell containing a known volume of liquid water to remove the dissolved CO_2. When the conductivity of the liquid water had stabilized, reagent C_2H_4 was added to the gas stream; the concentration range of C_2H_4 employed was 7-28 ppm. After the reaction was initiated by the addition of O_3 (concentration range: 0.5-1.0 ppm), the reaction mixture was analyzed for peroxide concentration at known time intervals using the HRPF technique. The concentration of peroxide of the reaction mixture was found to increase linearly with time (Fig. 11) and the reaction rate defined as

$$\text{Rate} = \frac{d[\text{peroxide}]}{dt} \tag{11}$$

was determined.

Assuming that the aqueous-phase reaction of O_3 and C_2H_4 is first order with respect to each reagent, eq. (11) is given as

$$\frac{d[\text{peroxide}]}{dt} = k_{12}\ [O_3]][C_2H_4] \tag{12}$$

Additionally, assuming that the liquid water is saturated with the reagent gases according to Henry's Law, i.e.,

$$[X] = H_x P_x \tag{13}$$

which allows eq. (12) to be rewritten as

$$\frac{d[\text{peroxide}]}{dt} = k_{12} H_{O_3} H_{C_2H_4} P_{O_3} P_{C_2H_4} \tag{14}$$

the second-order aqueous-phase rate constant k_{12} can readily be determined. The values of k_{12} determined at various reagent concentrations and pHs are

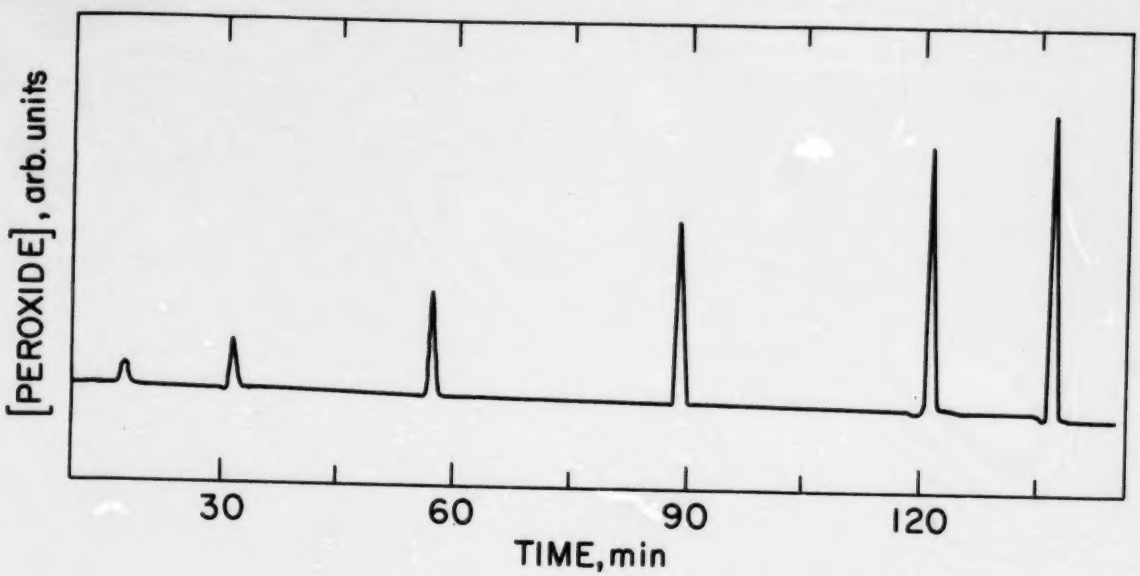

Figure 11. Time dependence of the concentration of peroxides as a reaction product in the O_3 - C_2H_4 reaction; p_{O_3} = 0.5 ppm and $p_{C_2H_4}$ = 28 ppm.

listed in Table 2. It should be noted that the average values were obtained from repeating runs as well as from runs with different reagent concentrations. The fact that the rate constant determined from eq. (14) remained essentially constant while the p_{O_3} and $p_{C_2H_4}$ were varied by a factor of 2 and 4, respectively, lends support to the assumed overall second-order kinetics.

For a gas-liquid reaction taking place in bulk liquid, particular attention has to be given to the mass transfer characteristics of the apparatus in order to identify the extent of mass transfer limitations on the

Table 2
Second-Order Rate Constant of Aqueous O_3-C_2H_4 Reaction*

pH	$10^{-5} \times k_{12}$, $M^{-1}\ s^{-1}$
neutral (6 ~ 7)	2.60 ± 0.26
5.0	3.0 ± 0.25
4.0	3.0 ± 0.23
3.0	3.3 ± 0.41

*[KCl] = 1×10^{-3} M, except for runs at pH 3; T = 22.0 ± 0.1°C.

overall reaction rates (Danckwerts, 1970). A simple approach to this identification is via the comparison of reaction time constant (τ_r) to the mass mass transfer time constant (τ_m): when $\tau_r \geq 10\ \tau_m$ the reaction is purely chemical reaction limited; when $\tau_r \not> 10\ \tau_m$ mass transfer will become a rate limiting process. For our currently employed gas-liquid reactor, the phase-mixing rate constant, k_m, was determined to be 0.47 s^{-1} (at liquid volume = 15 ml, total gas flow rate = 2.0 ℓ min^{-1}, cf. Lee and Schwartz, 1981). The time constants for the removal of aqueous O_3 and C_2H_4 by each

other are estimated as $\tau_{O_3} = (3 \times 10^5 [C_2H_4])^{-1} = 24$ s and $\tau_{C_2H_4} = (3 \times 10^5 [O_3])^{-1} = 300$ s. These reaction time constants are significantly longer than τ_m ($\triangleq k_m^{-1} = 2.14$ s); it is readily established that the chemical reaction is the rate limiting process and the reaction rate is not significantly affected by mass transfer processes. The assumption of the establishment of gas-liquid equilibrium is therefore validated.

From these results it is also seen that peroxide formation from the aqueous C_2H_4-O_3 reaction is independent of the solution pH,; the average rate coefficient $k_{12} = (3.0 \pm 0.3) \times 10^5$ M^{-1} s^{-1}, is applicable over the pH range 3 - 7. It should be noted that the fraction of organic peroxide formed in the C_2H_4-O_3 reaction was determined using the enzyme catalase technique in which the H_2O_2 is preferentially destroyed (Kelly et al., 1984; Schonbaum and Chance, 1976). The results of this test showed that $\gtrsim$60% (average of 3 runs made at pH 3) of the total peroxide was present as organic peroxide which appeared to be reasonably stable. The identity of the organic peroxide was not determined, but from the mechanism advanced for the formation of ozonide and Criegee radical, CH_3O_2H is considered a possible candidate.

Aqueous-phase Reactions of PAN

Peroxyacetyl nitrate (PAN), formed from the reaction of $CH_3C(O)O_2$ and NO_2, is an important atmospheric species because of its capacity as a reservoir for NO_2 and free radical species in transport processes. PAN was synthesized according to the method described by Nielsen (1982) and was stored in a heavy lipid, i.e., n-tridecane. Gas samples of PAN were prepared by mixing N_2 with the distillate from PAN/n-tridecane solution. With PAN vapor

pressure (over n-tridecane) in the order of 10 torr, 10 ppm gaseous PAN standards can be readily prepared. Because it was found that PAN decomposes on standing with a half-life of approximately 110 hrs (at 25°C, in the absence of NO, Senum and Gaffney, 1984), PAN standards were always freshly prepared for the same day use.

The three reactions of PAN examined include

$$\text{PAN(a)} \xrightarrow{k_{15}} \text{peroxide} \qquad (15)$$

$$\text{PAN(a)} + O_2 \xrightarrow{k_{16}} \text{peroxide} \qquad (16)$$

$$\text{PAN(a)} + O_3 \xrightarrow{k_{17}} \text{peroxide} \qquad (17)$$

The typical concentrations used for PAN, O_2, and O_3 were 100 ppb, 20%, and 1.0 ppm, respectively. Due to the low solubilities of O_2 and O_3, as well as of PAN (H_{PAN} = 3.6 M atm^{-1}, cf. Lee, 1984), these reactions were again studied by the use of the gas-liquid reaction cell described above. Final reaction mixtures (with total reaction time up to 1 hr) of these reactions were analyzed for peroxide and it was found that the levels of peroxide were all below the detection limit of our HRPF technique. Using a general rate expression

$$\frac{d[\text{peroxide}]}{dt} = k\ [\text{PAN}]\ [O_x] \qquad (18)$$

the upper limits for rate constants k_{15}, k_{16}, and k_{17} were estimated to be 2 x 10^{-4} s^{-1}, 3 x 10^{2} M^{-1} s^{-1}, and 3 x 10^{3} M^{-1} s^{-1}, respectively.

O_3 - NO_2 Reaction

In view of the suggestion that NO_3 is potentially important in cloud water chemistry (Heikes and Thompson, 1983), we have conducted some preliminary studies of $NO_3 + H_2O$. Since the solubility of NO_3 was not expected to be large, the reaction was carried out in the bubbler-type gas-liquid reactor into which the reagent gases were continuously replenished. Study of the background reaction involving H_2O and 1.3 and 43 ppm of O_3 showed that no detectable H_2O_2 was produced after 40 min of reaction. This result is consistent with that observed for the pure aqueous-phase O_3 decomposition study conducted in an optical cell (see above). To conduct the NO_2 experiment a pre-reaction chamber of 1-liter size was placed upstream of the bubbler to allow the production of NO_3 from the O_3- NO_2 gas-phase reaction. Since the second-order gas-phase rate constant for

$$O_3 + NO_2 \text{ --> } O_2 + NO_3 \qquad (19)$$

is 3×10^{-17} cm^3 s^{-1} (Baulch et al., 1982), the 1/e time for NO_3 formation is calculated to be 31 s at p_{O_3} = 43 ppm, the O_3 concentration employed. With 30 s residence time in the mixing chamber (total gas flow rates = 2 ℓ min^{-1}), nearly 70% of the NO_2 should be converted to NO_3 (p_{NO_2} employed was 40 ppb). It should be noted that the experimnets were carried out in the dark in order to avoid the photolysis of NO_3. At the end of 40 min the reaction mixture in the gas-liquid reactor was analyzed for H_2O_2 content. Concentration of H_2O_2 was found to be $\sim 1 \times 10^{-7}$ M. This low concentration seems to indicate that NO_3 has a limited role in the direct aqueous production of peroxide, at least in pure water and under neutral pH.

O_3-NO_2-H_2CO Reaction

Reactions of NO_3 with atmospheric constituents have been found to be important in nighttime chemistry (see, for example, Pitts et al., 1984). Since NO_3 can react with aldehydes to initiate free radical chain reactions, we have tested the possibility of the formation of peroxide by the aqueous reaction of NO_3 and H_2CO. In our approach, NO_2 (40 ± 1 ppb) and O_3 (40 ± 1 ppm) in N_2 (with 2% O_2) were allowed to react in a pre-reaction chamber (ca. 1 ℓ size) for ~30 s before entering the gas-liquid bubbler that contained 20 mℓ of a 1.0×10^{-4} M H_2CO solution. According to our calculation given in the previous section, nearly 70% of the NO_2 should be converted to NO_3. The reaction extent of the formaldehyde solution was followed by the peroxide concentration determined by an aliquot method. Despite the long reaction time (up to 100 min) no discernible peroxide was detected as a product.

DISCUSSION

A number of selected aqueous-phase reactions of O_3 have been studied in this research project. The main purpose of this work is to identify and characterize those aqueous O_3 reactions that would produce either hydrogen peroxide or organic perioxides as reaction products. Since the effort was mainly directed at the identification of those reactions, the entire project was scoping in nature; rather than spending a great length of time to characterize the detailed kinetics of a reaction which does not produce peroxide, we tried to maximize the number of reactions to be examined for peroxide production. As a consequence, the kinetic information obtained here with limited variations in reaction conditions are necessarily not comprehensive. For instance, reagent concentration variations were generally limited, the solution acidity was normally confined between neutral and pH 3, and the temperature was fixed either at 22.0 ± 0.1°C or room temperature. Nevertheless, we have attempted to make use of the data obtained in this work to qualitatively assess the atmospheric importance of these aqueous-phase O_3 reactions to the formation of peroxide and to the depletion of the reagent species.

O_3 Decomposition

Despite the fact that the kinetics of O_3 decomposition in aqueous solutions have been studied extensively, no agreement was reached with respect to its reaction order. The reaction order reported in the literature ranged from 1 (for example, Sullivan and Roth, 1979) to 2 (for example, Gurol and Singer, 1982), with some as 3/2 (for example, Kilpatrick et al., 1956). This discrepancy was suggested to result from a number of possible sources

such as mass transfer limitations, ionic strengths, impurities, as well as effects of buffers with which the solution pH were adjusted. The main features of O_3 decomposition observed in this current study are in agreement with some of the recently published results: (1) O_3 decomposition is insensitive to pH in the acidic region (Gurol and Singer, 1982), (2) decay of O_3 is first order in O_3 concentration (Sullivan and Roth, 1979), and (3) the first order rate constants determined in this work, i.e., 2.1×10^{-4} s^{-1} at neutral pH and 1.4×10^{-4} s^{-1} at pH = 2, are within a factor of 2 of those determined by Sullivan and Roth (1979), i.e., 4.1×10^{-4} s^{-1} and 2.4×10^{-4} s^{-1} for pH = 4 and 2, respectively. It should be noted that the aqueous-phase concentrations of O_3 used in this study were smaller than those used in previous studies by a factor of at least 10, and, therefore, may more closely resemble the actual atmospheric conditions. Using the aqueous-phase decomposition rate expressed as the gas-phase reaction rate (Lee and Schwartz, 1981), i.e.,

$$-\frac{p_{O_3}}{dt} = k\, H_{O_3} p_{O_3}\, LRT \qquad (20)$$

where L is the liquid water content of the atmosphere (volume fraction), we estimated the reaction time constant of O_3 against aqueous-phase decomposition to be 5×10^6 hr or longer for solution pH of neutral or lower at $L = 10^{-6}$. If wall effects in the laboratory study are partially responsible for the O_3 decomposition, then these estimated time constants would represent lower limits, rendering the atmospheric self-decomposition of O_3 in aqueous droplets even less important.

O_3-H_2O_2 Reaction

O_3 decomposition is known to be initiated by OH^- ion under basic conditions (Gurol and Singer, 1982; Sullivan and Roth, 1979; Staehelin and Hoigne, 1982). According to Staehelin and Hoigne, the conjugate base of H_2O_2, i.e., HO_2^-, also reacts with O_3 to produce free radicals such as $OH\cdot$ and $O_2\cdot^-$. From studies made in alkaline solutions, the rate constant for the O_3 - HO_2^- reaction, defined as

$$-\frac{d\,[O_3]}{dt} = k_{21}\,[O_3]\,[HO_2^-] \qquad (21)$$

was given as $(2.8 \pm .5) \times 10^6\ M^{-1}\ s^{-1}$. Replacing $[HO_2^-]$ with the total analytical concentration of H_2O_2, $[H_2O_2]_T$, we obtain

$$-\frac{d[O_3]}{dt} = k_{21}\,\frac{K_a}{K_a + [H^+]}\,[O_3]\,[H_2O_2]_T \qquad (22)$$

$$= k_{21}'\,[O_3]\,[H_2O_2]_T$$

where K_a is the acid dissociation constant of H_2O_2. For $pK_a = 11.6$ and pH = 6, k_{21}' is calculated to be $7.0\ M^{-1}\ s^{-1}$. This value is significantly smaller than that determined here; it is therefore concluded that the second-order rate constant determined in this study may reflect the direct reaction of O_3 and H_2O_2. The lower rate constant determined at pH 4 maintained with $[HCl] = 1 \times 10^{-4}$ M is qualitatively consistent with a negative $[H^+]$ dependence, although the possibility that the lower rate constant resulted from Cl^- ion inhibition (Taube and Bray, 1940) can not be excluded.

The fact that H_2O_2 can be destroyed by O_3 requires the effect of this O_3-H_2O_2 reaction on H_2O_2 concentrations be quantitatively assessed. To evaluate the time constant for the removal of H_2O_2 by the O_3-H_2O_2 reaction, we employ

$$\tau_{H_2O_2} = (k_{23}\ [O_3])^{-1} = (k_{23}\ H_{O_3} p_{O_3})^{-1} \quad (23)$$

With p_{O_3} = 1 ppm, $\tau_{H_2O_2}$ is calculated to be 10 hr at neutral pH and 660 hr at pH 4. These time constants are apparently too long to be important for our current laboratory studies.

The time constant for removal of atmospheric gas-phase O_3 by the aqueous O_3-H_2O_2 reaction is given as

$$\tau_{O_3} = (k_{23}\ H_{O_3}\ [H_2O_2]\ LRT)^{-1} \quad (24)$$

For $[H_2O_2] = 3 \times 10^{-5}$ M, a representative summer cloudwater H_2O_2 concentration (cf. Kelly et al., 1984), and $L = 10^{-6}$, τ_{O_3} is calculated to be 1.4×10^4 hr and 1.0×10^6 hr at neutral pH and pH 4, respectively. Since the aqueous-phase O_3 concentration in atmospheric water is significantly smaller than that of H_2O_2, the removal of the dissolved atmospheric H_2O_2 by the aqueous-phase O_3-H_2O_2 reaction will be extremely slow.

O_3-HCO_2H Reaction

Kinetics of this aqueous-phase reaction have been reported. Kuo and Wen (1977) found that the rate of O_3-HCO_2H reaction is first order with respect to $[O_3]$, and is dependent on $[HCO_2H]$ to the 1.2 power. The rate constant defined by

$$-\frac{d[O_3]}{dt} = K_{25}\,[O_3]\,[HCO_2H]^{1.2} \qquad (25)$$

was determined as 2.6×10^2 and 8.7×10^3 M^{-1} s^{-1} at pH 2 and pH 7, respectively. These values, along with an additional measurement at pH 11, showed a pH dependence in which the rate constant is approximately proportional to $[OH^-]^{1/2}$. Although the rate constant at pH 7 is in reasonable agreement with that determined in this work, i.e., 4.3×10^3 M^{-1} s^{-1}, the pH dependence of the reaction rate is quite different from that observed here.

The results reported by Hoigne and Bader (1983a), on the other hand, exhibited a pH dependence similar to that observed in this work, i.e., the rate law is consistent with a mechanism for which the reacting species consists of the dissociated formate ion rather than the undissociated formic acid. The rate constant reported by them for the O_3-HCO_2^- reaction was 140 M^{-1} s^{-1}, which is a factor of 28 smaller than that determined in this work. Their smaller value may very well have resulted from the doping of the reaction mixture with propanol, a free radical scavenging material. According to Hoigne and Bader, the presence of such a substance serves to inhibit the O_3 decomposition via free radical pathways. However, it may be somewhat uncertain whether the scavenger itself may enter the reaction pathways and whether certain scavengers may be more efficient than others.

Using the expression given by Eq. (4), the reaction time constants referred to gas phase for O_3 and HCO_2H against reaction (1) are estimated as

$$\tau_{O_3} = \left[k_4\left(\frac{K_a}{[H^+]+K_a}\right) H_{O_3}\, H_{HCO_2H}\, P_{HCO_2H}\, LRT\right]^{-1} \qquad (26)$$

and

$$\tau_{HCO_2H} = [k_4 \left(\frac{K_a}{[H^+]+K_a}\right) H_{O_3} H_{HCO_2H} P_{O_3} LRT]^{-1} \quad (27)$$

Using H_{HCO_2H} = 230 M atm^{-1} (at pH 4, Gaffney and Senum, 1984) and the following conditions: pH = 4, L = 10^{-6}, P_{O_3} = 50 ppb, P_{HCO_2H} = 10 ppb, and T = 25°C, $_{O_3}$ and $_{HCO_2H}$ are calculated to be 2.4 x 10^5 hr and 4.8 x 10^4 hr, respectively. These values are clearly too long to make this reaction significant.

O_3-H_2CO Reaction

Kuo and Wen (1977) studied this reaction and reported an O_3 decomposition rate which is dependent on $[H_2CO]$ to the first power and on $[O_3]$ to the 1/2 power. The rate constant defined by

$$-\frac{d[O_3]}{dt} = k_{28}[O_3]^{1/2}[H_2CO] \quad (28)$$

changed from 2.2 x 10^{-2} M$^{-1/2}$ s^{-1} to 0.53 M$^{-1/2}$ s^{-1} as pH increased from 2.7 to 7.2. On the other hand, Hoigne and Bader (1983b) suggested an overall second-order reaction, first order in each reagent, for which the rate constant was determined to be 0.1 ± 0.03 M^{-1} s^{-1} at pH 2. In contrast to both of these rate laws, we have suggested a tentative rate law, namely, that given by Eq. (10) where the power dependences of the rate on $[O_3]$ and on $[H_2CO]$ are assigned as one-half. The discrepancies observed in these studies may result from the different reaction conditions employed. For example, Hoigne and Bader used a H_2CO concentration in the range of 6-70 x 10^{-2} M, which is higher than the concentrations used in this study by 3 to 4 orders of magnitude. Since it is known that some aliphatic alcohols can serve as free radical scavengers, the hydrolyzed formaldehyde, i.e.,

dihydroxymethane, might efficiently block the free radical pathways of this reaction and diminish the overall observed rate.

The fact that different kinetic behavior is observed for varied reaction conditions suggests that these observed rate laws may at best be applied to those conditions used and should not be extrapolated to conditions which are vastly different. Since the conditions employed in this study involved the lowest concentrations for both O_3 and H_2CO among these studies, the kinetic information obtained in this study may be used to estimate the reaction time constants of atmospheric O_3 and H_2CO against the aqueous O_3-HCHO reaction. For the following conditions, namely, pH = neutral, P_{H_2CO} = 10 ppb, P_{O_3} = 50 ppb, and L = 10^{-6}, these reaction time constants are found to be 6 x 10^6 hrs or longer. Again, it may be concluded that the aqueous-phase reaction of O_3 and H_2CO affects very little the atmospheric life times of these species.

O_3-C_2H_4 Reaction

Due to the low solubility of C_2H_4, this reaction was studied using a continuous flow technique with the gas-phase reagent concentrations maintained constant throughout the reaction course. The second-order aqueous-phase rate constant determined from the peroxide formation rate, i.e., 3 x 10^5 M^{-1} s^{-1}, was found to be of similar magnitude to those determined for some substituted ethylenes such as 1-hexene-4-ol (2 x 10^5 M^{-1} s^{-1}) and styrene (3 x 10^5 M^{-1} s^{-1}) studied as homogeneous aqueous-phase reactions (Hoigne and Bader, 1983b). It is interesting to note that the substituent effect observed for the gas-phase O_3-olefin reactions seems to be absent in the aqueous phase.

The rate of depletion of O_3 and C_2H_4 from the gas phase due to aqueous O_3-C_2H_4 reaction may be estimated from

$$\tau = (k\, H_{O_3}\, H_{C_2H_4}\, LRT\, p)^{-1} \qquad (29)$$

For $p_{C_2H_4}$ = 20 ppb, p_{O_3} = 50 ppb, and L = 10^{-6}, the values of τs are found to be in the order of 1 x 10^7 hr. Evidently, these long reaction time constants would have minor consequences on the atmospheric residence times of either O_3 or C_2H_4.

The aqueous-phase rate of peroxide production from this reaction is estimated to be 6 x 10^{-11} M hr^{-1} for p_{O_3} = 50 ppb and $p_{C_2H_4}$ = 20 ppb. It should be noted that the O_3-olefin reaction will not constitute an important source of aqueous-phase peroxide unless the condition $(Hp)_{olefin} >$ 1 x 10^{-4} M is met. The current knowledge, however, indicates that such a species is not to be found (NSF, 1977).

Aqueous-Phase PAN Reactions

The contribution of aqueous-phase PAN reactions to peroxide production in the atmosphere can be estimated from the upper limits assigned to reactions (15) to (17). For a typical ambient condition where p_{O_3} = 50 ppb and p_{PAN} = 2 ppb, the upper limits of the rate of peroxide formation are evaluated as 4 x 10^{-9}, 1 x 10^{-6}, and 4 x 10^{-11} M hr^{-1} for PAN hydrolysis, O_2-PAN, and O_3-PAN reactions, respectively. The atmospheric residence times of PAN against hydrolysis, O_2-PAN, and O_3-PAN reactions under the same conditions and L=10^{-6} are found to be 2 x 10^4, 1 x 10^2, and 7 x 10^7 hr, respectively. Since these time constants are all significantly longer than the

typical cloud lifetime of ~1 hr (Pruppacher and Klett, 1978) and also longer than that for the gas-phase PAN-NO reaction, it is concluded that the atmospheric lifetime of PAN is not affected by these reactions.

O_3-NO_2-H_2CO Reactions

NO_3 has been examined extensively as an intermediate of the nighttime chemical transformations of nitrogen oxides (Winer et al., 1984). This species is suggested to be not only the source of HNO_3 but also a free radical initiator (Calvert and Stockwell, 1983), even for cloudwater droplets during the daytime (Thompson, 1983). According to the studies made in this work, no peroxide was found to be produced in the NO_2-O_3-H_2O reaction system regardless of whether H_2CO was present. In the case of NO_3 reacting with water the upper limit for the reaction

$$NO_3 + H_2O \xrightarrow{k_{30}} NO_2 + H_2O_2 \qquad (30)$$

can be estimated by equating the assumed rate expression

$$\text{Rate} = \frac{d[H_2O_2]}{dt} = k_{30}[NO_3] \qquad (31)$$

to the maximum possible rate estimated from the limit of detection of the HRPF method, i.e.,

$$k_{30}[NO_3] \lesssim 4 \times 10^{-11} \text{ M s}^{-1} \qquad (32)$$

It should be noted that the presence of high concentrations of O_3 (43 ppm) in these experiments might affect the aqueous-phase concentrations of H_2O_2 as it has been shown that their reaction can be rapid. From the rate

constants determined for the aqueous-phase O_3-H_2O_2 reaction the characteristic reaction times of H_2O_2 for $[O_3] = 4.7 \times 10^{-7}$ M are 13 min and 930 min at pH = neutral and 2, respectively. Although the O_3-H_2O_2 reaction is unimportant at pH 2, it may keep the $[H_2O_2]$ from building up at higher pH. If it is assumed that a steady-state concentration of H_2O_2 is established from the competing actions of O_3-H_2O_2 reaction and reaction (30), we may observe the following relationship, i.e.,

$$\frac{k_{30}\,[NO_3]}{k_{21}'\,[O_3]} \leq 1 \times 10^{-7}\ M \qquad (33)$$

For the conditions applied in this work, the inequality, $k_{30}\,H_{NO_3}\,P_{NO_3} \leq 1.2 \times 10^{-10}\ M\ s^{-1}$ is obtained. Using the previously calculated value for P_{NO_3}, the product $k_{30}\,H_{NO_3}$ is estimated to be $4 \times 10^{-3}\ M\ atm^{-1}\ s^{-1}$ or smaller. Although this value is approximately three times greater than that calculated from Eq. (32), the contribution of reaction (30) to the peroxide production in the cloudwater is still negligible, being only $5 \times 10^{-8}\ M\ hr^{-1}$ at P_{NO_3} = 3 ppb.

In the examination of the aqueous-phase reaction of NO_3 with H_2CO, the reaction between O_3 and H_2CO may consume the available H_2CO. According to Eq. (10), the rate of H_2CO disappearance due to reaction (5) is calculated to be $1.5 \times 10^{-7}\ M\ hr^{-1}$ for P_{O_3} = 43 ppm and $[H_2CO] = 1.0 \times 10^{-4}$ M. This rate is too small to influence the aqueous-phase concentration of H_2CO.

An upper-limit of the rate of the aqueous-phase reaction

$$NO_3 + H_2CO \xrightarrow{k_{34}} \text{Peroxide} \qquad (34)$$

can therefore be estimated from

$$\frac{d[\text{Peroxide}]}{dt} = k_{34}\,[NO_3]\,[H_2CO] \qquad (35)$$
$$= k_{34}\,H_{NO_3}\,P_{NO_3}\,[H_2CO]$$
$$\leq 1.7 \times 10^{-11}\ M\ s^{-1}$$

using the limit of detection of HRPF, i.e., 1×10^{-7} M. The product, $k_{34}\,H_{NO_3}$, was calculated to be smaller than 6 $atm^{-1}\ s^{-1}$. For the condition where P_{NO_3} = 3ppb and P_{H_2CO} = 20 ppb, the rate of peroxide formation in the aqueous-phase is estimated to be 8×10^{-9} M hr^{-1}. Again, this rate is found to be unimportant. It should be noted that the NO_3 concentration used here was calculated from the known kinetic information and has not been verified by an analytical method such as a spectrophotometric technique. Although our approach might suffer from interferences such as wall effects or the formation of N_2O_5, the experimental arrangement nonetheless mimics the bubbler H_2O_2 sampling methodology which manifested the artifact production of peroxide.

Aqueous-Phase H_2O_2 Formation

Although it has been suggested that aqueous-phase reactions of O_3 might be responsible for the *in situ* production of H_2O_2 in the bubbler experiments, the reactions examined in this work thus far did not provide evidence to support this contention. The maximum rate of peroxide formation of the reactions studied in this work, under typical atmospheric conditions, is found to be smaller than 1×10^{-6} M hr^{-1}. Naturally, the calculations were made for pure water systems and the possible effects of, say, metal ions have not been included. This conclusion may not be at variance with the observations reported by Heikes (1984), although the surface catalyzed O_3

decomposition leading to H_2O_2 production was not observed in our pure systems, where pure gases, instead of ambient air, were used.

One reaction which might produce H_2O_2 in the aqueous phase is the recombination of the dissolved HO_2 and its conjugate base O_2^-, i.e.,

$$HO_2 + O_2^- \xrightarrow{k_{36}} HO_2^- + O_2 \qquad (36)$$
$$\downarrow \text{fast}$$
$$\rightarrow H_2O_2$$

Using the Henry's law coefficient of HO_2 (2×10^3 M atm^{-1}) and rate constant k_{36} (1×10^8 M^{-1} s^{-1}) calculated from a thermochemical cycle (Schwartz, 1984) and pulse-radiolysis studies (Bielski, 1978), respectively, the aqueous-phase rate of H_2O_2 formation can be calculated from

$$\frac{d[H_2O_2]}{dt} = \frac{k_{36} K_a}{[H^+]} [HO_2] \qquad (37)$$
$$= k_{36}' H_{HO_2}^2 P_{HO_2}^2$$

where K_a is the acid dissociation constant of HO_2, being 2.0×10^{-5} M (Bielski, 1978). Accordingly, the gas-phase reaction time constant of HO_2 against reaction (36) is obtained as

$$\tau_{HO_2} = (2k_{36}' H_{HO_2}^2 P_{HO_2} LRT)^{-1} \qquad (38)$$

This quantity, calculated as a function of P_{HO_2}, is shown in Figure 12. These values, calculated under the assumption that the aqueous solution is saturated with the solute HO_2 according to Henry's law, suggest that the aqueous-phase recombination of HO_2 is potentially important as a source for the aqueous-phase H_2O_2 when P_{HO_2} is equal to or greater than 2×10^{-12}

atm. It should be noted that the calculations made here are limited to a single pH, i.e. pH = pK_a, for simplicity. Additionally, it should be pointed out that a steady-state concentration of HO_2 has been assumed in these calculations. If the consumption rate of HO_2 of reaction (36) is significantly faster than the rate of HO_2 production, then the steady-state assumption may not apply and the rate of H_2O_2 production will be primarily controlled by the source rate of HO_2.

The aqueous-phase production rate of H_2O_2 from the gas-phase recombination of HO_2 is also shown in Figure 12. Here we used a second-order rate constant of 2.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} and have assumed that the incorporation of the H_2O_2 into the liquid phase is instantaneous. The liquid water content is again assumed as 10^{-6}. It is interesting to note that the acquiring of the aqueous-phase H_2O_2 from the reactions of dissolved HO_2 is nearly two orders of magnitude faster than that can be supplied by the concomitant gas-phase recombination reaction of HO_2. Clearly, laboratory studies have to be carried out to examine this potentially important source of aqueous H_2O_2.

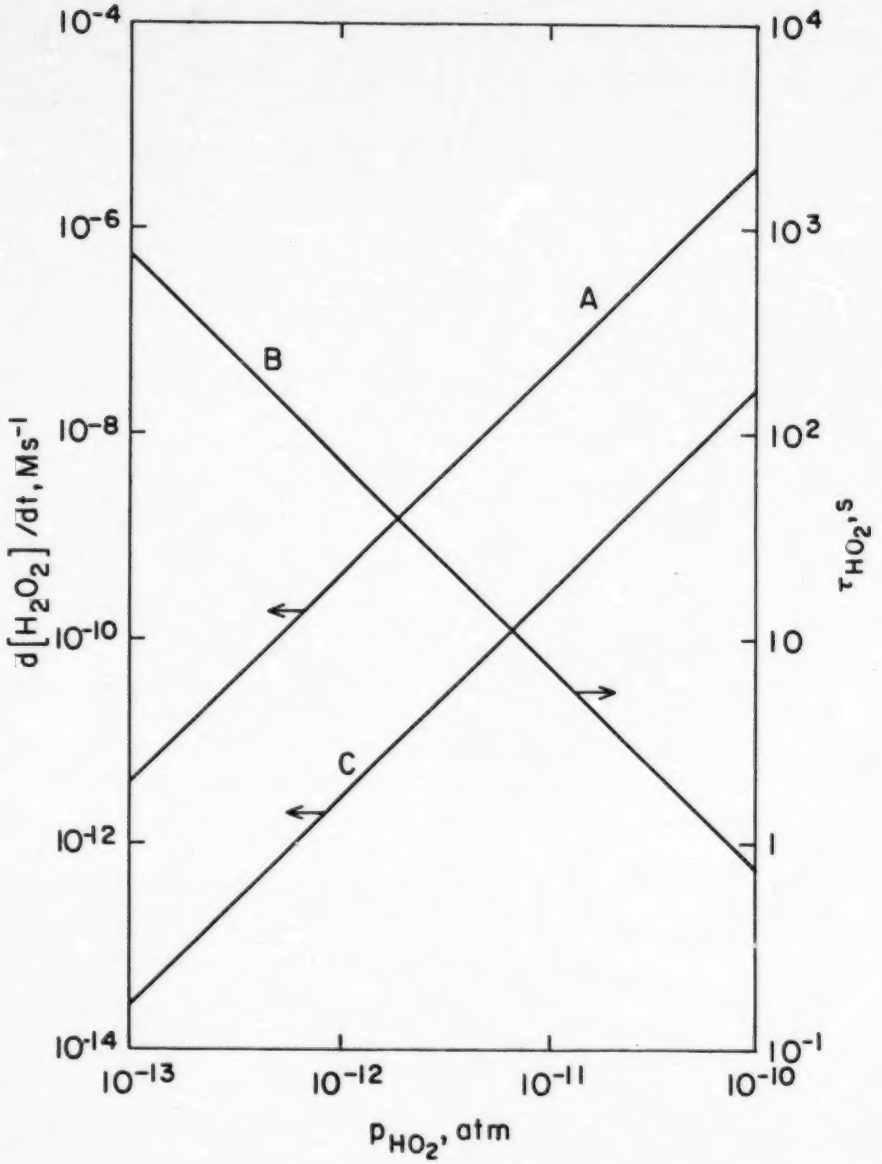

Figure 12. Contribution of the aqueous-phase HO_2 recombination reaction to the generation of H_2O_2, calculated for pH = 4.7. Line A represents the aqueous-phase rate of H_2O_2 production and line B the characteristic reaction time for gaseous HO_2 at $L = 10^{-6}$. Line C indicates the contribution to aqueous H_2O_2 from the gas-phase recombination of HO_2; H_2O_2 produced is assumed to be rapidly incorporated into the liquid water ($L = 10^{-6}$)

SUMMARY

Aqueous-phase reactions of O_3 with a number of important atmospheric components have been examined. Reaction kinetics and product analysis for hydrogen peroxide and organic peroxides were determined for the following reaction systems: (1) O_3 - H_2O, (2) O_3 - H_2O_2, (3) O_3 - HCO_2H, (4) O_3 - H_2CO, (5) O_3 - C_2H_4, (6) O_3 - PAN, (7) O_3 - NO_2, and (8) O_3 - NO_2 - H_2CO. The results obtained are listed in Table 3. Using these values calculations were made to estimate the atmospheric importance of these reactions to the removal of O_3 and the reagent species, as well as the production of peroxides in the liquid-phase. For typical atmospheric conditions (p_{O_3} = 50 ppb, $p_{H_2CO} \simeq p_{HCO_2H} \simeq p_{C_2H_4}$ = 20 ppb, p_{PAN} < 2 ppb, p_{NO_3} < 2 ppb, $L = 10^{-6}$, and pH = 2 ~ 6) it is concluded that none of these aqueous-phase reactions is important as a source of aqueous-phase peroxides or a sink for gaseous O_3 and its corresponding reagents.

Table 3
Summary of the Reaction Kinetics and Product Analysis
of Some Aqueous-Phase O_3 Reactions (22 ± 2°C)

Reaction System	Reaction Condition	$-\frac{d[O_3]}{dt}$	Yield or $\frac{d[\text{Peroxide}]}{dt}$	Rate Constant
$O_3 - H_2O$	$[O_3] \leq 2 \times 10^{-5}$ M	$k[O_3]$	$\leq 0.5\%$	2.1×10^{-4} s^{-1}, pH ~6 1.4×10^{-4} s^{-1}, pH = 2
$O_3 - H_2O_2$	$[O_3] \leq 2 \times 10^{-5}$ M $[H_2O_2] = 8\text{-}64 \times 10^{-6}$ M	$k [O_3][H_2O_2]$		2.6×10^3 M^{-1} s^{-1}, pH ~6 38 M^{-1} s^{-1}, pH = 4
$O_3 - HCO_2H$	$[O_3] \tilde{=} [HCO_2H]$ $= 1 \times 10^{-5}$ M	$k [O_3] [HCO_2^-]$	$\leq 0.5\%$	4.3×10^3 M^{-1} s^{-1} pH3 - 4.6
$O_3 - H_2CO$	$[O_3] \leq 2 \times 10^{-5}$ M $[H_2CO] = 4\text{-}17 \times 10^{-5}$ M	$k [O_3]^{1/2}[H_2CO]^{1/2}$	$\leq 2\%$	1.2×10^{-3} s^{-1}
$O_3 - C_2H_4$	$p_{O_3} = 0.5 - 1.0$ ppm $p_{C_2H_4} = 7\text{-}28$ ppm		$k [O_3][C_2H_4]$	3.0×10^5 M^{-1} s^{-1} pH 3-6
O_3 - PAN	$p_{PAN} = 100$ ppb $p_{O_3} = 1.0$ ppm		k [PAN] $[O_3]$	$\leq 3 \times 10^3$ M^{-1} s^{-1}
$O_3 - NO_2$	$p_{O_3} = 43$ ppm $p_{NO_2} = 40$ ppb		$k H_{NO_3} p_{NO_3}$	$k H_{NO_3} \ll 4 \times 10^{-3}$ M atm^{-1} s^{-1}
$O_3 - NO_2$ $- H_2CO$	$[H_2CO] = 1 \times 10^{-4}$ M	$k H_{NO_3} [H_2CO] p_{NO_3}$		$k H_{NO_3} \leq 6$ atm^{-1} s^{-1}

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